First Quarterly Report

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for

# DEVELOPMENT OF UNIFORM AND PREDICTABLE BATTERY MATERIALS FOR NICKEL CADMIUM AEROSPACE CELLS

Covering Period

May 8 through August 7, 1968

Contract No. NAS5-11561

Prepared by

Tyco Laboratories, Inc.
Waltham, Massachusetts 02154

for

National Aeronautics and Space Administration

Goddard Space Flight Center

Greenbelt, Maryland

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# ABSTRACT

The development of more reliable nickel cadmium batteries for aerospace application is dependent on improvements in the uniformity and reproducibility of the battery plates. It is the purpose of this program to study the sintering and plaque filling processes associated with plate manufacture in order to improve these factors.

The first report presents a survey of the literature pertaining to the manufacture of nickel cadmium battery plates and examines present industrial practices in this field, particularly quality control. The general conclusions are that the industry, though manufacturing a successful commercial product, is not geared to the production of high quality plates for aerospace application.

The experimental program to define the critical variables in the manufacturing process is outlined briefly.

A preliminary analysis of the uniformity of physical characteristics of several samples of the commercial nickel powder, exclusively used in battery plate manufacture, indicates variations in bulk density, surface area and particle size distribution. The grain size and Fisher number, however, show much less variation.

# ACKNOWLEDGMENTS

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# I. INTRODUCTION

The nickel cadmium couple is in principle ideally suited
to secondary battery application. The design, manufacture and
operation of nickel cadmium batteries is, however, anything but
straightforward. The long cycle life, which is the chief attractive
feature of the nickel cadmium battery, can only be demonstrated
at low depths of discharge and with limitations on the charge and
discharge rates. Under more demanding operating conditions,
reliability and life are severely reduced. Typical failure modes
are loss of capacity, high voltage on overcharge, and the generation
of $H_2$ on overdischarge. This behavior can be reasonably ascribed
to a lack of reproducibility and uniformity in battery plate structure.
Cell design and construction are also important in this context, since
cell clamping pressure and the properties of the separator may be
nonuniform. These factors will be considered in the future but are
not part of the immediate program. Each stage in the manufacture of
both nickel and cadmium battery plates will be examined to define
the important process variables and the degree to which they need
be controlled to obtain uniform electrode structures in a reprodu-
cible manner.

Considerable importance is attached to the requirement
for uniformity in the physical characteristics of individual battery
plates. The influence of uniformity on single cell or battery
characteristics is readily illustrated as follows.

Consider a straightforward example of a cell with electrodes
of the same total capacity in which the distribution of the active
materials is not uniform. At practically useful charge-discharge
rates, the cell geometry dictates that the active material on one
electrode can interact efficiently only with its mirror image in
the opposite electrode. The advantage of matched total capacity
is therefore lost when the active material is nonuniformly dis-
tributed. At 100% depth of discharge, based on the individual
plate capacities, the sequence of events depicted in Fig. 1    leads

# CHARGE-DISCHARGE CYCLE FOR NON UNIFORM ELECTRODES
## OF ONE CELL OF A NICKEL CADMIUM BATTERY
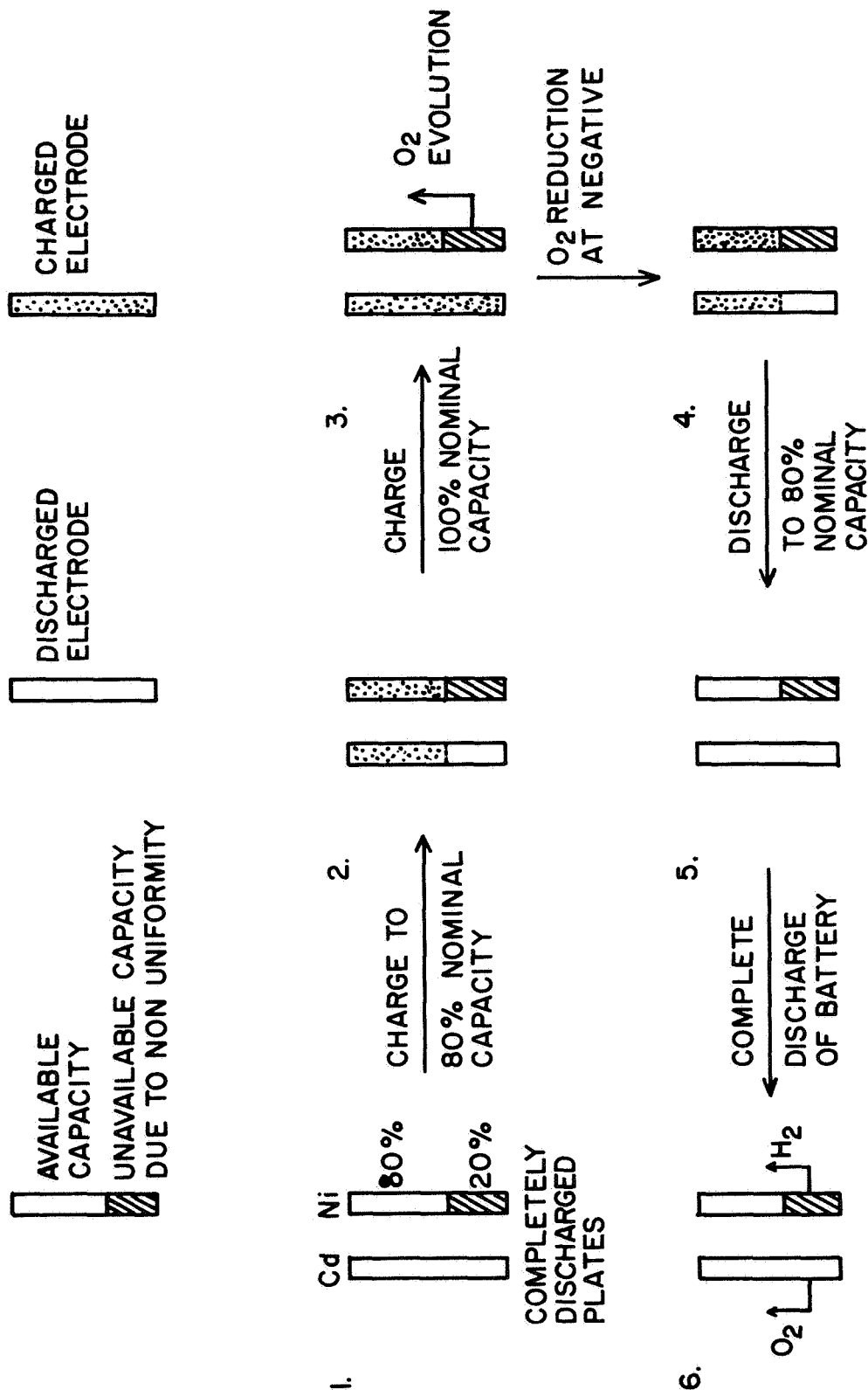
immediately to $H_2$ evolution. This can obviously be avoided by restricting the depth of discharge. If, however, the source of nonuniformity is more subtle (such as differences in pore size distribution or areas of high resistance in the porous nickel substrate), then cycling at even moderate depths of discharge can gradually reduce the available capacity. The capacity decreases because the inefficiencies in the charge and discharge processes are cumulative rather than complimentary. This behavior explains how cells chosen with matched capacities for battery construction can show different aging characteristics and thereby defeat the initial objective.

The expression "nonuniformity" is not very explicit, and it is important for later discussions to define in more detail the concepts as they apply to battery plate structure. It is not suggested, for example, that we try to achieve uniformity at the microscopic level, i. e. preparing electrodes from a nickel powder of uniform particle size to give a plaque with a uniform pore size. Because of the large number of pores per square centimeter and the extensive cross linking in the porous mass, the variation in pore size is averaged out; i. e. the attainment of microscopic uniformity is unnecessary. Similarly, one cannot expect uniform behavior in depth in the porous mass; the rate of the electrode reaction will vary with depth in the pore structure. Also, in normal operation the current density is not uniformly distributed over the electrode surface. What is essential is that the patterns of nonuniformity, the distribution functions in depth or over the surface, should be identical from point to point on the surface and from electrode to electrode. These requirements will follow if the more general requirement of macroscopic uniformity, the focal point of our analysis, is met. By macroscopic uniformity we mean that any segment of the electrode (say of the order of 1 $cm^2$ of the surface) should display identical physical characteristics to any other segment. It is one of the

main purposes of this program to define which of the character-
istics such as porosity, pore size distribution, surface area,
conductivity, amount of active material, etc., are critical to
the uniform behavior of the electrode.

As the first phase of the program, this report reviews
the processes involved in battery plate fabrication and discusses
the present practices in the areas of process control and quality
assurance. In addition, the proposed experimental approach to
the study of plate fabrication procedures and the development of
nondestructive testing methods is outlined.

## II.  THE BASIC OPERATIONS OF NICKEL CADMIUM BATTERY PLATE MANUFACTURE

### A.  Introduction

This review of the fabrication of nickel and cadmium battery plates is based on the information available in the open literature. It should be noted that much of the literature on the sintering of metal powders is related to the production of materials with very low porosity.  Whereas this information was examined, it is not reviewed here since it is considered to be irrelevant to the production of highly porous nickel plaques.

The general background and the historical development of the nickel cadmium battery are readily available in several authoritative reviews by Vinal[1], Thomas and Milner[2] and Atkinson[3]. A comprehensive bibliography of the literature pertaining to secondary aerospace batteries is to be published shortly by Halpert and Webster[4].

The basic operations of nickel cadmium battery plate manufacture of relevance to present day practice were first described by Fleischer[5].  Several other workers, including Tracey, et al[6]; Worn and Perks[7]; Hancock, et al.[8]; Menard[9]; Jost and Popat[10]; and Johnson and Nietzel[11] have made detailed studies of various aspects of the process.  These are most conveniently discussed as follows under the headings of nickel powder characteristics, the sintering process to produce a porous nickel plaque, and impregnation of the plaque with active materials.

### B.  Nickel Powders for Battery Plaque Manufacture

The objectives in the manufacture of porous nickel plaque for battery use are, in general terms, 80% porosity, good mechanical strength and conductivity with uniform thickness and pore size distribution.  Nickel powders must therefore have a bulk density $<\sim 1.0$ g/cm$^3$ and sintering characteristics that will provide the necessary strength and conductivity.

The principal commercial sources of nickel powder suited to battery plaque manufacture are the International Nickel Co., Inc. (the nickel carbonyl process) and Sherritt Gordon Mines, Ltd. ($H_2$ reduction of aqueous nickel ammonium carbonate). Alternative sources of powder specifically for battery plaque manufacture have been considered by Appelt, et al.[12] (electrolytic powders), and by Justi[13] (the addition of Raney nickel to carbonyl nickel). Schwank, et al.[14], claim that the addition of finely divided NiO nickel powder makes sintering possible at temperatures close to 300°C (cf. 800-900°C for conventional sintering processes and 500°C by Appelt).

Several grades of powder prepared by the carbonyl process are available. Types 123 and 128 are described[15] as "spiky equiaxed granules," and types 255 and 287 are composed of chainlike structures of irregularly shaped particles. The last two figures in each of the type designations represent a typical apparent density figure (e.g. 2.3 g/$cm^3$ for 123 and 0.55 g/$cm^3$ for 255). The first figure distinguishes the shape factors discussed above. The main characteristics of these powders are given in Table I. The particle size ranges from 1 to 20 $\mu$, with some filamentary particles considerably longer.

The spiky nature of the powder particles is apparent in the scanning electron micrographs presented in the NASA Goddard Internal Document (X735-68-400) distributed simultaneously with this report. (Note that some sintering of the surface could take place in the electron beam, resulting in the rounding off of some of the spikes.) The interlocking of these surface spikes, coupled with the filamentary nature of the powder, no doubt contributes to bridging mechanisms that give rise to sintered plaques of high porosity without the use of spacing agents.

The filaments are, however, relatively fragile (though the spikes are not easily broken) so that extensive mechanical handling results in an increase in apparent density. In practice, this means that the apparent density must be determined immediately prior to use. The physical characteristics of these powders result in poor flow characteristics that give rise to extensive nonuniformity in loose sintering techniques[20].

# TABLE I

Physical Characteristics of International Nickel Co.

Carbonyl Nickel Powders[1]

| Powder Type | Bulk Density, $\Delta g/cc$ | Average[2] Particle Size, Microns | Typical Analyses, weight % | | |
| --- | --- | --- | --- | --- | --- |
| | | | C | O | S |
| 255 | 0.45- 0.6 | 2.6⁻ 3.4 | 0.1 | 0.1 | 0.0002 |
| 287 | 0.8 -1.0 | 2.9⁻ 3.6 | 0.1 | 0.1 | 0.0002 |
| 100 | 1.6 -2.0 | 3-5 | 0.15 | 0.1 | 0.0002 |
| 123 | 2.0 -2.5 | 4-7 | 0.08 | 0.1 | 0.0002 |
| 128 | 2.5 -3.0 | 7-9 | 0.05 | 0.1 | 0.0002 |
| 337 | 3.5 -4.0 | ------- | 0.08 | 0.25 | < 0.001 |

(1) From INCO brochure, Carbonyl Nickel Powders, January 1967.

(2) By Fisher Subsieve Sizer

Tracey has also described experimental carbonyl powders with the same filamentary structure as the 255 and 287 powders but with a smooth surface. These powders have not been made available commercially.

Nickel powders prepared by precipitation and reduction in ammonium carbonate show a wide range of characteristics compared with the carbonyl powders. According to Kunda, Evans and Mackiw[16] the morphology can vary from dendritic to trigonal or rhombohedral, according to the preparative conditions. Furthermore the apparent density of the powder may be controlled by varying the $NH_3/Ni$ molar ratio. For low apparent densities the $CO_2/Ni$ ratio must also be maintained below 0.5. Powders of totally different characteristics are obtained on precipitation from nickel ammonium sulphate, but these powders contain too high an impurity level of Fe and S (ferrous sulphate is needed as a nucleation catalyst in this reaction) to permit the use of these powders in Ni/Cd battery plaques. The important physical characteristics of the commercially available powders[17] G 08 and G 09 are given in Table II. Earlier work on Sherritt Gordon powders and on nickel oxide as a starting material was described by Casey, Bourgault and Lake[18].

Appelt, Dominiczak, Nowacki and Paskiewicz[12] compared carbonyl nickel powder (type 287), nickel powder produced by the decomposition of nickel formate, and electrolytic nickel. The authors claim that the electrolytic powder may be used to produce porous nickel plaques that are comparable with those prepared from carbonyl nickel powder. No tests of impregnated battery plates are presented. The maximum porosity of the plates sintered at 500° and 700°C was 54.5%. The electrolytic powder showed, in photosedimentation measurements, a wider particle size range than the carbonyl nickel powder. For the sintering tests the powder was classified into three groups; the two fractions

## TABLE II

Physical Characteristics of Sherritt Gordon "G" Grade*
Powders

| Powder | G09 | G08 |
|---|---|---|
| Apparent density, g/cc | 0.92 | 0.83 |
| Tap density, g/cc | 1.24 | 1.13 |
| Fisher number | 5.1 | 3.1 |
| Surface area, $m^2/g$ | 0.43 | 0.64 |

Chemical Analysis, %

| | | |
|---|---|---|
| Nickel and cobalt | 99.9 | 99.9 |
| Cobalt | 0.042 | 0.065 |
| Copper | 0.004 | 0.005 |
| Iron | 0.008 | 0.007 |
| Sulphur | 0.005 | 0.003 |
| Carbon | 0.011 | 0.020 |
| $H_2$ loss | 0.36 | 0.48 |

* From reference 8.

with the larger particles were used for the sintering tests. The formate nickel powder showed very few particles > 10 $\mu$ and a peak in the distribution at 2 - 3 $\mu$, with an apparent density of 0.32 g/cm$^3$.

The electrolytic powder showed particles from 5 to > 25 $\mu$ with a peak at 12 $\mu$ and an apparent density of 0.9 g/cm$^3$. The carbonyl nickel powder had a much sharper distribution, with a peak between 12 and 15 $\mu$.

In no case among the references cited has any property of the powders been identified as being of particular importance in controlling the character of the sinter. However, in the case of dense coatings produced by the sintering of nickel powder, Handwerk and Sanborn[19] have taken into account the influence of changes in powder morphology and apparent density from batch to batch of INCO type 123 carbonyl nickel powder . In an effort to com - bine these two effects into a single measurement for formulation and quality control purposes, they have defined an apparent surface area expressed as

$$\frac{\text{Apparent surface}}{\text{area cm}^2/\text{g}} = \frac{10^4}{\text{Fisher size } (\mu) \text{ x apparent density (in g/cm}^3)} \quad *$$

Using this figure as a guide, reasonable constancy of viscosity of the slurried powder was achieved for wide ranging powder characteristics.

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* The Fisher size is an air permeability figure that measures the external or frictional surface of the powders. This figure is of more significance in sintering kinetics than the BET area which includes the internal porosity of the powders as well as the external surface. These factors are discussed in more detail later.

The principal general conclusions that can be stated with regard to the choice of nickel powders for sintered battery plaques are as follows:

(a) Low bulk density is essential.

(b) Filamentary shapes are preferred.

(c) Powders of low surface area (i. e. little internal porosity) give less shrinkage.

(d) Relatively high purity is required (particularly with regard to Fe and S content).

More specific comments than these cannot be made until the sintering process is discussed, since most of the literature describes a particular combination of powder type and sintering process.

## C. Nickel Plaque Fabrication

### 1. Production of the Green Plaque

The first stage of the preparation of a uniform porous sinter from the powder is the formation of a uniform green plaque. The four principal methods of green plaque formation are listed below and are subsequently discussed from the point of view of uniformity.

(a) Loose or gravity sintering

(b) Slurry coating techniques

(c) Roll compaction

(d) Die pressing.

The emphasis on the commercially available powders in this discussion reflects the greater attention they have received in the literature.

The loose sintering process involves the sieving of a powder of a specific bulk density into a mold leveling the mold and subsequently sintering. Sieving through a 400 mesh sieve is reported[21] to produce an improvement in uniformity by reducing the range of pore sizes from 10 - 300 $\mu$ to 10 - 25 $\mu$.

The bulk density must be controlled in order to obtain a specified porosity in the plaque. Since variations in bulk density can occur for carbonyl powders during handling and shipping (as discussed above), the first step of a loose sintering process is the blending of different batches of powder to give a bulk density that will give rise to the desired porosity on sintering. This practice is a potential source of nonuniformity and irreproducibility from plaque to plaque in terms of the other important physical characteristics such as surface area and grain size. As mentioned previously, the filling and particularly the leveling of the mold, is a serious source of nonuniformity in loose sintering. The incorporation of a central support in the plaque is mandatory in battery applications to give mechanical strength and good electrical conductivity. This further complicates the loose sintering technique from the point of view of uniformity. Two filling and two leveling processes are then required. The support, however, reduces the volume shrinkage on sintering and prevents the enhancement of any nonuniformity in the green plaque.

The slurry technique is based on the dip coating of a mesh or perforated strip of nickel with a suspension of nickel powder in a solution of methyl cellulose, a wetting agent and an anti-foaming agent. The methyl cellulose is burned off in the sintering process, leaving a highly porous nickel plaque. The success of the method, judged by good adhesion to the support and a crack and tear free film, is dependent on close control of the viscosity of the slurry, and in maintaining all the solids in suspension. This method has the particular advantage of providing the filamentary carbonyl powders with good flow characteristics, thereby avoiding the uniformity problem associated with mold filling in the loose sintering technique. Plaque thickness is relatively easy to define. Some difficulties may be expected due to the presence of dissolved air. Vacuum degassing is recommended[19] in the formation of dense

coatings to prevent bubble formation and subsequent porosity. Bubble formation could be a source of nonuniformity in battery plaques. The porosity of the plaque is still dependent on the bulk density of the powder even in the presence of a binder. Careful control of the bulk density of the powder is still essential for reproducible plaques. If the blending of powder batches is used to achieve a specified bulk density, then the same problems of uniformity of surface area and grain size occur as were discussed under the heading of loose sintering.

Roll compaction requires a uniform feed of a uniformly mixed nickel powder and spacing agent between two accurately aligned rollers. Since uniform mixing of powders suitable for the preparation of high porosity plaques is difficult and local agglomeration results in hard spots, uniform plaques are not easily produced. It is particularly difficult to prepare highly porous structures because of the low mechanical strength of the green plaque. The presence of a mesh support included in battery plaques helps to improve the mechanical strength and also permits the use of smaller rollers (2" instead of 8" diameter, an important economic factor). The porosity is affected by roll size and roll speed, the gap between the rolls and the amount of spacing agent. According to Tracey[22] the maximum porosity that can be achieved by this method is 70% in the absence of a support mesh. Since the support mesh enhances densification, 70% porosity in the presence of a mesh could only be achieved with greater roll separation, i. e. plaque thicknesses > 0. 040 in. Plaques thicker than 0. 040", particularly with the broad distribution of pore size that roll compacting produces, are not normally considered suitable for battery application. However, a later paper of Tracey[23], with less detailed description and discussion, claims that satisfactory battery plaques can be prepared. Roll compaction of Sherritt powders has been described by Blore, et al.[24]; their conclusions are essentially similar to those arrived at for carbonyl powders.

Die pressing has also been shown to be unsuited to the production of high porosity sintered plques, largely because of low green strength.

## 2. The Sintering Process

In the second stage of the process the green plaque is converted into a mechanically strong support for the active material by sintering. The principles underlying the mechanism of sintering of metal powders to give rigid bodies with varying degrees of porosity were first described by Kuczynski[25].

In the formation of a highly porous nickel sinter we are interested only in the initial stages of densification, that of neck growth. Four transport mechanisms can contribute to neck growth: plastic flow, evaporation and condensation, volume diffusion and surface diffusion. These mechanisms can be separated experi- mentally by the equation

$$\frac{x^n}{a^m} = F(T) \cdot t.$$

where x is the radius of the neck, a is the radius of the particle, T is the temperature and t the time, n and m are rate parameters given by the following for the various mechanisms.

$$n = 2 \quad m = 1 \qquad \text{for plastic flow}$$
$$n = 3 \quad m = 1 \qquad \text{for evaporation and condensation}$$
$$n = 5 \quad m = 2 \qquad \text{for volume diffusion}$$
$$n = 7 \quad m = 3 \qquad \text{for surface diffusion}$$

In the preparation of nickel sinters for battery plate application, we are primarily concerned with the latter two mech- anisms. It may be noted that volume diffusion results in shrinkage but surface diffusion does not. Quantitative interpretations of the sintering of nickel powders, particularly those with the complex surface structures and shapes of the carbonyl powders, are unlikely but the theory provides a good basis for understanding the physical changes that occur. For this reason we have not included in this review the literature relating to the densification of near spherical powders by sintering.

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### 3. Plaque Characteristics as a Function of the Sintering Process

The characteristics of plaques prepared from carbonyl nickel has been extensively studied by Tracey and co-workers. The most detailed study[20] was of the loose sintering process in which four powders with bulk densities of 0.60, 0.85, 0.90 and 0.98 g/cm$^3$ and with varying impurity levels were examined for varying sintering times and temperature and sintering atmosphere. The plaques were characterized by porosity, volume shrinkage, linear shrinkage, mechanical strength, and resistivity measurement. Surface area and pore volume distribution were also examined on a slightly less comprehensive level.

The major conclusions can be summarized as follows:

(a) After the first 15 min. there is little change in total porosity with sintering time. There is, however, some coalescence which results in the growth of large pores at the expense of small ones. (This behavior has only a small influence on the shape of the pore volume distribution curve but is readily identified in the photomicrographs.) The elimination of small pores by extended sintering could give rise to more uniform plates. Johnson and Nietzel[11] report that pores less than 7 $\mu$ are not corroded during the impregnation process; i.e. there is little active material in these pores. They recommend pore formers rather than extended sintering times to eliminate small pores "since the pore volume does not necessarily have to be sacrificed." Tracey's work indicates that this loss is < 2%. Since the conductivity and mechanical strength increase significantly for longer sintering times, these approaches appear advantageous.

(b) Volume shrinkage can range from 20 to 40%. The major change was reported in the thickness, though the change in width of a 2 - 1/2" x 3/4" plate was also significant. A difference in behavior between the length and the width shrinkage (the length

shrinkage is small) was attributed to frictional effects rather than to any anisotropy related to mold filling. The fact that the top surface shrank more than the bottom confirms this interpretation. Almost all the shrinkage occurred in the first few minutes of sintering and can be explained by a "bedding down" of the powder as the surface roughness is removed. The longitudinal shrinkage cannot be explained by this mechanism and must be attributed to volume diffusion into the initial bonds formed by the surface processes. In the presence of a support mesh, only depth shrinkage occurs; the above observations, in the absence of a support mesh, give important pointers to the mechanism of the sintering of carbonyl nickel powders.

(c) Increasing the sintering temperature in the range 700 - 1000°C had the effect of decreasing the porosity. Up to 900°C the effect was small ( < 5%), but at 1000°C the decrease in porosity, particularly at long times, was significant ( > 10%). As might be expected, the depth shrinkage increased markedly with increase in temperature.

(d) The mechanical strength increased with sintering temperature, from ~ 10 kg/cm$^2$ at 700°C to > 50 kg/cm$^2$ at 900°C.

(e) Electrical resistivity was significantly higher at 700°C compared with the higher temperature values. Good correlation was found between resistivity and mechanical strength. Tracey concludes from these relationships for the four powders of varying bulk density that in the range of 80 to 90% porosity the highest strength and lowest resistivity were obtained with the powder of lowest initial bulk density.

(f) The surface area changes on sintering were studied for one of the powders. The results show an initial fall from 0.7 m$^2$/g to 0.38 m$^2$/g after 15 mins. at 800°C. An increase in surface area was observed at 30 min and 60 min (0.51 m$^2$/g

and 0.49 $m^2/g$, respectively) that Tracey does not interpret. A possible explanation for this increases is slow oxidation of the surface.

(g) The variation in carbon content of the four powders is apparently not an important factor in any of the physical changes studied.

(h) Three sintering atmospheres were examined: dry $H_2$, wet $H_2$ and cracked $NH_3$. Greater volume shrinkage was observed in wet $H_2$. The mechanical strength was lower and the resistivities higher in the case of cracked $NH_3$. There was little to distinguish between the properties of plaques produced in wet and dry $H_2$.

It is interesting to note, from the point of view of uniformity of behavior, that the four powders studied by Tracey and Perks[20] give rise to considerable differences in plaque characteristics. This is as true of the two powders with nearly equal bulk density (0.85 and 0.90 $g/cm^3$) as it is of any other combination. The authors do not discuss this point or consider what factors in the original powders give rise to these differences on sintering.

In a later paper Williams and Tracey[22] have extended their studies to plaques prepared by the slurry technique, by roll compaction and by pressing, though these studies are not so comprehensive as the loose sintering studied. For the slurry technique results are reported for type 255 and 287 powders sintered at 700, 900 and 1000°C for 15 min in cracked $NH_3$. The porosities are reported, "at a first approximation," to be of the same order as those of the loose sintering technique (typically 85% for loose sintering and 78% for slurry coating). For the slurry technique the mean pore size is somewhat smaller and there are fewer large pores. The pore size distribution is particularly sharp for the type 255 powder, which also shows slightly higher porosity - 78% compared to 74% for the type 287.

The resistivity of these two plaques was 95 $\mu$ ohm. cm (255) and
74 $\mu$ ohm. cm (287). Further improvement in the resistivity was
reported (74 → 60 $\mu$ ohm. cm) by sintering at 1000°C instead
of 900°C for only a 1% loss in total porosity. The electron
micrographs, however, show significantly more coalescence
of the nickel particles.

The plaques produced by roll compaction in the presence
of a space filler[22] (40% methyl cellulose by weight) achieve
porosities in the range 70 to 75% only when the sintering tem-
perature is restricted to 700°C for a relatively short time
(12 min), and by the use of a flat electroformed or expanded
metal mesh rather than the more usual woven mesh as the con-
ductive support. Under these conditions the bend strength and
electrical resistivity are comparable to plaques prepared by
the slurry process from the same nickel powder (type 287) at
900°C. Some densification and powder bonding can be expected
during the rolling process, permitting the use of lower sintering
times and temperatures. The method provides an economically
competative method of producing highly porous nickel plaque but
appears to be more difficult to control to achieve a very high
degree of uniformity, because of the requirement to keep the nickel
powder and space filler properly mixed right up to the compacting rolls.

No data exists in the literature on the sintering character-
istics of the smooth surface experimental powders mentioned
earlier in this review.

Hancock, Evans and Mackiw[8] have described the
physical characteristics of Sherritt Gordon G Grade nickel
powders and their relation to the properties of nickel plaques
produced by loose sintering for battery application. Four powders
were examined with bulk densities of 0. 58, 0. 77, 0. 83, and
0. 92 g/cm$^3$. Abrasion loss (a measure of mechanical strength),
porosity, resistivity and volume shrinkage were studied as functions
of the sintering time and temperature. The sintering atmosphere
was hydrogen.

These powders showed much greater variation in be-
havior than the carbonyl powders but showed exactly the same
trends. There was little variation of the above properties with
sintering time after 15 min; increased temperature, however,
produced a lower resistivity, greater strength and about a 5%
decrease in porosity in the range 800 - 1000°C. The resistivities
of these plaques in the absence of a supporting mesh tended to be
higher than those of the carbonyl powders for the same degree of
volume shrinkage. This difference would not be significant in the presence
of a supporting conductive mesh. The coalescence of the powders at higher
temperatures and longer times was very similar to the carbonyl powders.

Hancock, et al., also found that the tendency for these low
density nickel powders to shrink was related to their specific surface
area, a relationship that can be conveniently expressed in terms
of the Fisher number. The following empirical equation was
developed to predict the porosity of plaques sintered at 900°C for
20 min.

$$P = 100 - \frac{AD}{0.089 - 0.104 \, (FN)^{-1.2}}$$

P = porosity

AD = apparent density

FN = Fisher number.

The authors conclude that the most important characteristic
governing the strength and resistivity was the particle size. High
strength and low resistivity were claimed for much lower sin-
tering times and sintering temperature when the powder had a
small particle size. These conclusions are unsupported by ex-
perimental evidence; no measurements of particle size are
presented in the paper.

The capacity of plaques prepared from four powders of varying bulk density, sintered at 1000°F for 20 min and impregnated with $Ni(OH)_2$ at a loading of 1 g/cm$^3$ of pore volume, showed the expected increase with increasing porosity. The capacity was measured at the 1 hour rate.

Menard[9] has examined a series of powders from both the International Nickel Co. and Sherritt Gordon Mines. The bulk density of the initial powders ranged from 0.598 to 1.178 g/cm$^3$. The range was extended to 0.41 to 1.52 g/cm$^3$ by sieve separation. The principal conclusions were that the shrinkage on sintering at 930°C (no time specified) was highest for the lower bulk density powders and that the resistivity was largely independent of bulk density. From the limited detail in Menard's presentation (an extended abstract), it is not clear whether these conclusions were based on identical sintering operations or sintering to a pre-determined electrode porosity and thickness. It is separately reported that the porosity increases with decreasing bulk density and also that the porosity increases with plate thickness.

In the impregnation experiments, conducted with plates of constant thickness, the greatest capacity was observed for the most porous plates, but higher efficiency was noted for plates of lower porosity and particularly for plates that show a larger percentage of pores at the lower end of the distribution. From the pore spectra the most efficient plate is that in which > 80% of the pore volume of the plaque is below 7 $\mu$ dia. This differs from the viewpoint expressed by Johnson and Nietzel[11] quoted earlier, and that of Schneider[26] who states that the highest possible width of pore, coupled with a sharp pore spectrum, is desirable.

Appelt, et al.[12], prepared plaques from the following: carbonyl nickel powder, electrolytic nickel powder (two samples of different particle size distribution), and powder from the decomposition of nickel formate.

The plaques were described as suitable for application in the construction of Ni/Cd batteries, but the maximum porosity recorded was 54.5%. These low porosities at relatively low sintering temperatures (500°C and 700°C) are a result of pressing at 1 T/cm$^2$ immediately prior to sintering. This practice would also explain the low values quoted for volume shrinkage on sintering, which was 4.5% at 500°C and 10% at 700°C for the carbonyl nickel. (Most of the shrinkage observed in loose sintering is a "bedding down" of the powder as the surface roughness of the particles is eliminated.) The formate nickel powder, which had a significantly higher surface area, showed 37% shrinkage. The electrolytic powder showed 4% and 12% shrinkages, the higher figure being associated with the smaller particle size distribution. The maximum pore size was quoted as 1 $\mu$ for the carbonyl nickel and 0.64 and 0.25 $\mu$ for the two fractions of the electrolytic powder.

A tenfold change in grain size on sintering the carbonyl nickel probably the reflects the annihilation of the small surface crystallites which would have a pronounced effect on this average value derived from the X-ray measurements. At 500°C there is little change in the grain size of the formate nickel, but at 700°C there is a threefold change. This behavior agrees with that described by Evans and Ashell[27] who report that even though densification is greatest in the early stages of sintering significant grain growth is restricted to the later stages.

The work of Casey, Bourgault and Lake[18] examined Sherritt Gordon and INCO nickel powders ranging in bulk density from 0.73 to 4.5 g/cm$^3$. The powders were sintered in a mold with a light cover plate that produced a 20% compression of the powder. The optimum sintering conditions for each powder and for a 55% NiO/45% Ni powder (4.5 g/cm$^3$) mixture were given as 1050°C for 1 to 2 hours. The porosity was in each case 80%. The plates prepared from the plaques incorporating NiO disintegrated

after activation and cycling. The remainder of the plates showed equivalent performance, except that those prepared from carbonyl nickel were more efficient at high drain rates. This was attributed to a larger average pore size in the plaques prepared from the Sherritt Gordon powders.

Several other papers have described the fabrication of fuel cell electrodes in which uniformity of pore size is a critical factor. Among these are Bagshaw, Barnes and Evans[28]; Kravic[29]; Adams, Bacon and Watson[30]; Clarke and Kordesch[31]; and Drazic Despic and Vujcic[32]; Jung and van Dohren[33]. The manufacturing techniques do not contain any special techniques for achieving uniformity of pore size and are essentially the same as those already described above.

The concensus of opinion among the papers dealing with battery plaque manufacture is that optimum plaque characteristics are obtained from a powder with a low surface area, a bulk density as high as is compatible with the 80% porosity requirement, and sintering conditions that are vigorous enough to provide good mechanical strength and conductivity without sacrificing porosity. The importance of these characteristics will be more apparent after the discussion of the impregnation process.

### D. Impregnation with Active Materials

Uniformity of battery plate operation must eventually depend on a uniform distribution of the active materials throughout the plaque. Several methods are available for the precipitation of the active materials in the pores. Since they are not simple processes their influence on uniformity is difficult to assess. Chemical methods give higher capacity plates, but they are accompanied by extensive corrosion of the plaque. The loss of mechanical strength and conductivity that ensues could result in some of the improved capacity being unavailable at high drain rates. Electrochemical methods give lower capacity but the integrity of the plaque is less affected. Details of both approaches are discussed below.

The basic chemical method described by Fleischer[5] involves vacuum impregnation of the porous nickel with slightly acidified, near saturated solutions of nickel nitrate or cadmium nitrate. The nitrates are converted to the hydroxides by immersion in hot KOH with simultaneous cathodic polarization at a rate of 150 ma/cm$^2$. The procedure is repeated until sufficient uptake of active material has been achieved (four to ten cycles), leaving the plates with 40 to 50% residual porosity. Jost and Ruferacht[34] have shown that the sequential impregnations result in a sponge of discrete particles rather than a straightforward increase in crystallite size. The surface area was found to be directly related to the amount of Ni $(OH)_2$ in the plates.

The cathodization reduces the nitrate ions to $NH_4^+$, assisting the precipitation of the nickel or cadmium hydroxides. It is also an effective mechanism for removing nitrate ions which otherwise have a detrimental effect on battery operation by accelerating self-discharge. Without cathodization, the active material has a tendancy to be precipitated outside the plaque. A significant amount of the active material of the positive electrode is produced by direct corrosion of the plaque. The corrosion reaction is probable essential to good adhesion and hence good electrical contact of the active material to the porous nickel substrate. The plates are thoroughly washed after impregnation to ensure complete removal of KOH; residual KOH forms carbonate on contact with air and affects the performance and uniformity of behavior of sealed cells because of enhanced corrosion of the positive plates.

A variant of this process is described by Bourgault, Lake, Casey and Dubois[35] in which the nickel and cadmium nitrates used for plate impregnation are dissolved in their own water of crystallization by gentle heating. The nitrates are then decomposed thermally prior to treatment with KOH (in this case

without simultaneous cathodization). Sufficient active material is deposited in a single step. Nitrate ions, which as noted above have a detrimental effect on self-discharge rates, are essentially eliminated during the thermal treatment. It is claimed that there is no loss of active material during immersion in the KOH. The extent of corrosion of the plaque is dictated by the contact time of the nitrate melt with the plaque prior to thermal decomposition. In measurements with nickel plaques, possessing far from optimum pore structure, it was noted that the active material was deposited preferentially close to the surface of the plaque leaving the center void; if this behavior is a general one, then this process would enhance any nonuniformity in the plaque.

In the Kandler process[36] the precipitation of the hydroxides is achieved by cathodizing the porous plaques in nickel or cadmium nitrates. The nitrate ion is reduced to form ammonium hydroxide, which then precipitates the active material. Since the local pH controls the precipitation, the reaction is initiated at sites with the longest diffusion path from the $H^+$ ions of the bulk electrolyte, i. e. deep in the pores of the electrode. The completion of the impregnation process can be recognized by the onset of a green coloration at the surface of the electrode. Hausler[37] has examined the effectiveness of this method of impregnation as a function of the various plaque characteristics. The main points are that plaques with a sharp pore size distribution and with very few narrow mouthed pores are preferred. Hausler argues against the use of roll compacted material, if this method of activation is to be used, since there is greater densification at the surface in contact with the rollers and thus poor penetration of the pores. The presence of a binder as in the slurry process results in open pores because of the escaping gases during sintering. Greater uniformity of deposition, together with greater activity of the $Ni(OH)_2$ so formed, is obtained at room temperature rather than elevated temperatures. The total capacities are somewhat lower than those obtained with other processes.

McHenry[38] has also described this process for production of positive active material. Details of the effect of temperature and current density on the distribution of active material are given. Uniformity of the current density is described as essential, otherwise the plates warp. Uniformity of deposition of the active material is controlled to better than $\pm$ 2%, and from this point of view the process looks attractive.

Kober[39] has described a method of impregnating positive plates electrolytically by cathodization in ammine nickel formate in the presence of KOH. Current interruption is used to improve the uniformity of the deposit, and high capacity plates are claimed. Carbonate is produced in the anodic process by the oxidation of formate; (the anode and cathode were separated by a Dacron diaphragm in Kober's work). Attempts to use the ammine nickel sulfate were unsuccessful. The black oxide is formed which precipitates at the surface of the plates. The amine formate method apparently has the advantage that there is very little corrosion of the nickel plaque during impregnation.

The anodic oxidation of nickel plaques in sodium bicarbonate to form the positive active material has been described by Schneider[26]. The process is claimed to be successful in practice, as long as strong sintered plaques with a narrow pore spectrum but wide pores are used. The capacities, however, are low and since the active material is derived from the porous plaque, it is inevitable that the plaques are weakened.

In addition to the pasted or electrodeposited cadmium electrodes, several alternative methods are available for the preparation of negative electrodes dependent on the porous nickel support structure. As examples of electrolytic methods, Henderson[40] has described the conditions under which a spongy deposit of cadmium can be electroplated on to Ni, a similar process has also been reported by Bogenschutz and Jentzsch[41]. Thermal decomposition of cadmium acetate to the oxide has been proposed by Wagner[42].

## III. CURRENT PRACTICES IN THE PRODUCTION OF Ni/Cd BATTERY PLATES

### A. Introduction

This survey is based on discussions held with the major manufacturers of Ni/Cd batteries in the United States. The discussions were restricted to nonproprietary aspects of battery plate fabrication. Quality control procedures and the influence of process variables on the uniformity of the final product were emphasized in the discussion. With the exception of the comments on the production of carbonyl nickel by the International Nickel Co., Inc. (INCO), this presentation is made in general terms without explicit reference to any manufacturer.

We will first consider the starting materials for the process and then discuss the production process and quality control procedures.

### B. Choice of Starting Materials

All manufacturers at present use INCO carbonyl nickel powders (type 255 and 287) for plaque fabrication. These powders are well suited to battery plaque manufacture but their unanimous selection is based entirely on economic considerations. The carbonyl powders are prepared by a batch process; the various batches are air blended to meet the bulk density ranges defined for the two types of powder. Since the bulk densities change on shipment due to the fragile nature of the filamentary particles, it is standard practice for each manufacturer to measure the bulk density of the powder immediately prior to use.

The batches are blended, if necessary, to obtain the bulk density specified for each manufacturer's process. (For constant sintering conditions plaque porosity is inversely related to powder bulk density.) Bulk density then is the only physical characteristic of the powder that is monitored by either the powder manufacturer

or the user. Consequently, the porosity is the only factor con-trolled in the plaque. It is acknowledged that variations can occur in grain size, particle size distribution, surface area and carbon content of the carbonyl powders. These factors can in-fluence the pore size distribution, internal surface area, con-ductivity, etc., of the plaque as is discussed in the previous sections. The other choice facing a battery plate manufacturer is the nature of the conductive support for the porous nickel.

The alternative forms of support for the porous mass are nickel (or nickel plated) screen or perforated sheet. Nickel screen is the preferred choice in most cases but plates for prismatic cells prepared by the SAFT method are based on perforated sheet. Adhesion of the porous mass to the support is considered to be better for the screen but the perforated sheet provides better current distribution at high drain rates. There is a plainly visible decrease in thickness in the regions of the perforations in the sheet electrodes. A marked difference in the character of the porous mass would be expected in these regions, i. e. the plates are inherently nonuniform. In practice it is easier to control the thickness and flatness of the plates based on perforated sheet. Nickel screen is usually stretched and rolled flat as the first stage of the continuous production of the plaque.

### C. The Production Process

One of the most interesting features of Ni/Cd battery manufacture is that an acceptable product is obtained from several very different techniques, with wide ranging values of the process variables. Obviously no single step in the process is critical and we might expect the fabrication of battery plates to be straightforward. This is not so in practice, mainly because of the complex interactions between the successive stages of the process; (the nature of these interactions is discussed earlier in this report). Thus, even though the process variables differ from

manufacturer to manufacturer, the values within a particular sequence are critical. A successful production process is largely dependent on maintaining the delicate balance between each stage of the process.

The over-all picture then is of an inflexible production process completely unsuited to conventional methods of process control. Operating normally the process will produce to specification, but once perturbed, there is no single variable that can be adjusted to correct the deviation. Also, the rate of feedback of information from the slow moving production process is not fast enough to be very effective in practice. The tests carried out in production are essentially quality assurance. In the following analysis we will discuss those process variables which can be routinely controlled by the manufacturer and the quality assurance tests that are available.

The battery manufacturers are unanimous in their choice of the slurry technique for the production of porous nickel plaque. The preference for this method over loose sintering or roll compaction is based on the relative ease with which it is operated as a continuous process. It also has the advantage that the poor flow characteristics of the carbonyl nickel powders that give rise to poor reproducibility and uniformity in the other methods are circumvented.

In this process it is essential to control the bulk density of the powder, the viscosity, temperature and pH of the slurry and the time and temperature of sintering. A more reproducible product is achieved if the sintering atmosphere is kept constant. Several of the manufacturers monitor its composition. A better quality plaque is claimed for processes in which the methyl cellulose is burned off under controlled conditions immediately prior to sintering. Burn off at the sintering temperature can result in carbon deposition and surface oxidation by the decomposition products of the methyl cellulose. Surface oxidation followed by

reduction in the sintering atmosphere creates local increases
in surface area. Enhanced corrosion occurs in these regions
of high surface area during impregnation producing areas of lower
mechanical strength and higher resistivity. None of the manu-
facturers of battery plates consider   vacuum degassing of the
slurry to be important. This is essential in the preparation of
dense nickel coatings using the same basic techniques. Without
degassing, air bubbles can cause blisters during the drying
process. The blisters are an obvious source of nonuniformity.

The quality assurance tests routinely carried out in the
plaque are visual inspection, thickness, weight per unit area
(porosity) and a measurement related to the conductivity (typically
the hardness). Different specifications exist for the positive and
negative plate material. Commercially, more attention is paid
to thickness than any other variable. In many cases it is mon-
itored continuously on the production line. The specifications of the
nickel plaque used for the manufacture of the batteries for the
Telstar satelite are quoted as an example in Table III.

More sophisticated tests that are made in some cases are
the pore size distribution, the surface area and the uniformity of
weight per unit area. This last test is the only one in which the
distribution of physical characteristics is considered. In the
measurements of pore size distribution, plaques are rejected if
too great a percentage of their pore volume falls below a particular
figure. As noted previously the internal surface area influences
the extent of corrosion during impregnation.

The impregnation process is probably the most critical
stage in the preparation of battery plates and the one in which
there is the most art. Of the methods reviewed in the early sections
of this report, only two are used in practice. The first involves
successive vacuum impregnations with solutions of the nitrates
followed by cathodization in KOH; the second is the one-step
process of impregnation with "molten" nitrates which are thermally

## TABLE III

Specifications of Battery Plates used on the Telstar Satelite[43]

| | |
|---|---|
| Positive plate thickness | $0.0249 \pm 0.0005$ in. |
| Positive plaque porosity | $79.8 \quad \pm 0.4\%$ |
| Negative plate thickness | $0.0200 \pm 0.0007$ in. |
| Negative plaque porosity | $78.2 \quad \pm 0.6\%$ |

decomposed prior to treatment in KOH. Both methods give high capacity plates and both are characterized by extensive corrosion of the plaque. In some cases the cadmium electrodes are prepared by totally different techniques that do not depend on a porous nickel structure.

Among the factors routinely controlled in these processes are the purity of the starting materials (the nickel and cadmium salts, the quality of the deionized water, etc.) , and bath composition, temperature and pH. Stringent precautions need to be exercised in the handling and storage of the Ni plaque prior to impregnation. Oxidation by the corrosive atmosphere surrounding the impregnation process or the accumulation of a grease film from the atmosphere can affect the wetting characteristics of the plaque. Even after vacuum impregnation, solutions are rejected from hydrophobic pores. Cathodization in KOH is an effective cleaning process that finds limited application in practice.

Great care is necessary in washing to remove KOH between the successive impregnations in the first method listed above. Without effective washing, the active material is precipitated in the mouth of the pore blocking further impregnation. A final wash is essential to prevent carbonate formation in the pores prior to cell assembly. The handling and drying of the plates at this stage can affect the quality. After drying, the plates are brushed lightly to remove excess surface material. Note that sodium hydroxide is used in place of potassium hydroxide by many manufacturers because it is cheaper. (Forming must, however, be carried out in potassium hydroxide. )

A number of quality assurance tests carried out on the final plates varies from manufacturer to manufacturer. In some cases it is restricted to weight gain on impregnation; (good agreement between weight gain and capacity is readily established experimentally). Direct measurement of the charge/discharge characteristics at various drain rates and temperatures on sample plates

can be used to provide more comprehensive information. Where
a high drain rate and long life are looked for, it is important to
measure the extent of corrosion during impregnation. In this
case the active material is dissolved out and the weight loss
of the plaque measured. Tests for residual nitrate content
are routinely made by some manufacturers. Note that none of
these tests are nondestructive in nature.

In summary, the processes currently used to prepare
Ni/Cd battery plates to close specifications do not offer much
flexibility in operation. Careful control of the process variables
is essential in order to meet these specifications. The reliability
of the product is dependent on the effectiveness of the quality
assurance tests. At present these are carried out on samples
taken from the production process; i.e. there are no non-
destructive tests of quality and no tests of plate uniformity.
These last two factors are considered to be the key to improved
reliability, and for this reason they are the main objectives of the
experimental effort in this program.

The over-all impression of the industry is of a technology
that has taken a fundamentally rugged and reliable electrode couple
and produced a battery that is commercially viable in the consumer
market. In achieving this, several short cuts are taken in the
production process. Reversing this approach to obtain a completely
reliable product for more sophisticated application is a very
difficult task. But as work in a related field (the preparation of
porous nickel for the Apollo fuel cell electrodes) has shown, it is
possible to prepare highly reliable materials by careful analysis
of the problems and close attention to detail.

## IV. PHYSICAL CHARACTERISTICS OF NICKEL POWDERS

As indicated in the previous section, carbonyl nickel powders obtained from the International Nickel Company are the starting materials for all porous nickel production for battery plate application. It was also established that the only quality control test on the powders by both the manufacturer and the user was the measurement of the bulk density. Since other physical properties of the powders are also important in determining the characteristics of the sintered plaque, we have examined the extent to which these properties vary from batch to batch of the INCO powders. For comparison, we also include two powders manufactured by Sherritt Gordon Mines, Ltd.

Samples of carbonyl nickel powder were obtained from INCO and from each of the battery manufacturers visited in the course of the industrial survey in order to obtain a representative cross section.

The measurements made were bulk density, surface area, particle size distribution, Fisher number, and average grain size. The results are presented in Tables IV and V.

The bulk density measurements were made by the ASTM method (B 212-48, 1965). Ten determinations carried out on samples of 704-14 and 704-15 showed rms deviations of 0.008 and 0.007 $g/cm^3$, respectively. The measurements in Table IV are based on three concordant determinations so that we may conclude that observed differences are real and not a function of sampling or experimental error. The type 255 powders of nominal bulk density 0.55 $g/cm^3$ gave values between 0.61 and 0.68 $g/cm^3$; the type 287 with a nominal bulk density of 0.87 $g/cm^3$ showed values from 0.91 to 1.07 $g/cm^3$. As discussed earlier, larger values of the bulk density are to be expected for those samples that have been extensively handled; e.g. the powder obtained in a small lot directly from INCO (704-1) showed a lower bulk density than those obtained from the battery manufacturers.

## TABLE IV

### Physical Characteristics of Various Nickel Powders[1]

| | Surface Area $m^2/g$ | Bulk Density $g/cm^3$ | Grain Size $\overset{o}{A}$ | Fisher Number[2] ($\mu$) |
|---|---|---|---|---|
| 704-1 | 0.386 | 0.91 | 449 | 3.22 |
| 704-2* | 0.535 | 0.68 | 369 | 2.82 |
| 704-3* | 0.540 | 0.61 | 392 | 2.63 |
| 704-4 | 0.394 | 1.02 | 458 | 3.27 |
| 704-5 | 0.420 | 1.07 | 474 | 3.21 |
| 704-6 | 0.454 | 1.07 | 450 | 3.23 |
| 704-7 | 0.386 | 1.01 | 447 | 3.39 |
| 704-8 | 0.446 | 1.04 | 449 | 3.18 |
| 704-9 | 0.471 | 0.99 | 456 | 3.15 |
| 704-10 | 0.457 | 0.97 | 494 | 3.18 |
| 704-11 | 0.429 | 1.02 | 436 | 3.18 |
| 704-12 | 0.437 | 0.98 | 457 | 3.16 |
| 704-13 | 0.405 | 0.97 | 452 | 3.23 |
| 704-14* | 0.507 | 0.68 | 384 | 2.78 |
| 704-15 | 0.446 | 0.99 | 424 | 3.14 |
| 704-16+ | 0.756 | 0.95 | 406 | 2.17 |
| 704-17+ | 0.496 | 0.99 | 390 | 3.58 |
| 704-18 | 0.448 | 0.99 | 464 | 3.51 |

(1) Most of the powders examined are INCO Type 287, those marked * are INCO Type 255, and those marked + are Sherritt Gordon powders.

(2) With the exception of 704-9 these measurements are in accord with those presented in the NASA Goddard Document X 735-68-400 which accompanies this report.

Since it is routine practice for manufacturers to blend powders to a specified value of the bulk density, we will examine the variation of the other physical properties as a function of the bulk density; i. e. we will determine whether blending will also compensate for variations in physical properties other than bulk density.

The surface areas, listed in Table IV, determined by the BET method using Kr, show no regular variation with the bulk density. Among the type 287 samples, the powder with the lowest bulk density showed the lowest rather than the highest area. The measurements are reproducible to $+ 5\%$ (0. 02 $m^2/g$) for repeat measurements on the same powder sample and from sample to sample of the same powder, so that the values recorded for the 287 powders represent real differences in surface area. The surface area of the 255 powders (mean value of 0. 53 $m^2/g$) is significantly higher than that of the 287 powders (mean value 0. 43 $m^2/g$). The blending of the two types of powder to obtain a specified bulk density would obviously give rise to wide variations in powder surface area. It is part of our experimental program to determine the significance of variations in surface area on sintering characteristics.

The measurements of the Fisher number, which is more likely to be significant in determining sintering characteristics, do not show as much variation as the BET surface area. The reproducibility of the Fisher number assessed above as a combination of sampling and experimental error is $\pm 0. 03$ $\mu$. With two exceptions (704-4 and 704-7) all the results for the 287 powder fall within a limit, 3. 19 $\pm 0. 05$ $\mu$. The 255 powders show a greater spread of values, ranging from 2. 63 $\mu$ to 2. 82 $\mu$. The observed differences for both types of powder showed no correlation with bulk density.

The particle size distribution was determined by a cumulative sedimentation technique, using a commercially available accessory to the Cahn electrobalance. The median particle size was reasonably uniform in the vicinity of 12 $\mu$; details are shown in Table V. The one exception to the above comment was the

## TABLE V

Particle Size Distribution Determined by Sedimentation in 32% Glycerol in Water

| Sample # | Median diameter μ | Weight Percentage Distribution | | | | | | | | Total % <21 μ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 5-7 μ | 7-9 μ | 9-11 μ | 11-13 μ | 13-15 μ | 15-17 μ | 17-19 μ | 19-21 μ | |
| 704-1 | 15.8 | 4 | 7.5 | 9 | 10.5 | 13 | 12.5 | 11 | 11 | 88.5 |
| 704-2* | 12.8 | 7.5 | 10 | 15 | 16.5 | 15 | 12 | 9 | 7 | 93 |
| 704-3* | 13.4 | 7 | 9 | 12 | 15 | 20 | 15 | 11 | 8 | 97 |
| 704-4 | 12.0 | 8 | 13.5 | 17 | 18 | 18.5 | 14.5 | 8 | -- | 97.5 |
| 704-5 | 12.8 | 7.5 | 10 | 15 | 16 | 17 | 13 | 11 | 9 | 98.5 |
| 704-6 | 12.2 | 5 | 12 | 17 | 19.5 | 18 | 16.5 | 9 | -- | 97.0 |
| 704-7 | 12.2 | 10.5 | 12.5 | 13.5 | 17.5 | 20 | 15 | 8 | -- | 97 |
| 704-8 | 11.5 | 8 | 15 | 17 | 19 | 20 | 13 | 3 | -- | 95 |
| 704-9 | 11.7 | 8.5 | 13 | 17.5 | 18 | 18 | 15 | 5 | -- | 95 |
| 704-10 | 12 | 5 | 12 | 16 | 24 | 22 | 11 | 4 | -- | 94 |
| 704-11 | 12.4 | 8 | 13 | 13 | 16 | 15.5 | 15 | 11 | 4 | 95.5 |
| 704-12 | 12.2 | 7.5 | 12 | 15.5 | 18 | 17.5 | 16 | 10 | -- | 96.5 |
| 704-13 | 11.7 | 9.5 | 13 | 18.5 | 18.5 | 18.5 | 14.5 | 3 | -- | 95.5 |
| 704-14* | 12.0 | 9 | 12.5 | 15 | 17 | 19 | 20 | 3.5 | -- | 96.0 |
| 704-15 | 12.7 | 8 | 11 | 12.5 | 14.5 | 15 | 13 | 10 | 10 | 94.0 |
| 704-16+ | 11.7 | 11.5 | 13 | 17.5 | 19 | 17 | 14 | 7.5 | -- | 99.5 |
| 704-17+ | 15.2 | 7.5 | 8 | 10 | 11 | 12 | 12.5 | 11 | 13 | 83.0 |
| 704-18 | 11.4 | 12.5 | 13.5 | 16 | 19.5 | 20 | 14 | --- | -- | 95.0 |

*INCO Type 255 - +Sherritt Gordon powders.

sample received directly from INCO (704-1) which had a median particle size of 15. 8μ. It is also significant that this sample had 11. 5% of its particles > 21μ; (21μ was the upper limit of detection under experimental conditions). Packaged as a small sample, at the source of manufacture, this powder was subject to less vigorous mechanical disturbance which has resulted in less damage to the larger filamentary particles. The numerical values for the percentage distribution by weight from sample to sample for the same powder were not very reproducible, but the shapes of the distribution curve were not significantly different. The shapes of the distribution curves from powder to powder are sufficiently different to warrant consideration as a variable in the sintering process. No distinction can be drawn between the distribution curves of the 255 and 287 powders. Note also that the particle diameters are very different from the equivalent spherical diameter, the Fisher number. This difference reflects the filamentary shape of the particles.

The measurements of average grain size by X-ray line broadening on random samples of the same powder showed reproducibility to better than $\pm$ 4%. For the 287 powders, there is no evidence of variation in average grain size. The mean value of 454 $\overset{\circ}{A}$ is significantly greater than that of the 255 powders showing a mean value of 382 $\overset{\circ}{A}$.

In summary, the type 287 powders show real differences in surface area and particle size distribution that can not be related to the variations in bulk density. The magnitude of these differences is not great but could be important in defining the sintering behavior of the powders. Little or no difference could be detected in average grain size and Fisher number. The 255 and 287 powders are quite different in physical characteristics. Indiscriminate blending of these two types of powder is considered to be a likely source of irreproducibility and nonuniformity.

## V. EXPERIMENTAL PROGRAM

The objectives of this program are to identify and eliminate the sources of variability and nonuniformity in the fabrication of Ni/Cd battery plates.

The prime variables associated with each stage of the manufacture of Ni/Cd battery plates are indicated in the accompanying chart, Fig. 2. The possible interactions and interrelations of these variables are indicated by broken lines. The selection of the slurry method for the manufacture of nickel plaque using INCO carbonyl nickel powders is based on the conclusions of the survey presented in an earlier section of this report.

The experimental approach will consist of a series of factorial experiments to establish near optimum processes for producing both positive and negative plates, and to define which of the process variables have the greatest influence on the physical characteristics of the plate.

At each stage of the process the product will be examined for uniformity. A correlation will be looked for between any observed nonuniform characteristics and the variables of the process.

It is considered that the experimental techniques used to define plaque and plate uniformity are potentially useful as non-destructive quality control tests.

The first objective must be to prepare a uniform plaque, which in turn requires uniformity in those physical characteristics of the nickel powder important to the sintering process.

The first task, for which preliminary results are reported in the previous section, is an analysis of the extent of variability in the physical characteristics of several samples of carbonyl nickel powders. In the continuation of this work in the next report period we will seek to define the influence of these variables and of the sintering conditions on the nature and uniformity of the sintered plaque.

SINTERING PROCESS

Powder: Surface Area, Bulk Density, Grain Size, Air Permeability, Particle Size Distribution, Particle Morphology

Slurry: Viscosity, Wetting Characteristics

Sintering: Time, Temperature, Atmosphere, Burn off of filler

Plaque: Thickness, Surface Area, Pore Size Distribution, Conductivity, Mechanical Strength, Nature of Conductive Support

IMPREGNATION

Method of Activation, Amount of Active Material, Pore Structure, Extent of Plaque Corrosion, Conductivity, Mechanical Strength

TESTING

High charge/Discharge Rates, Low charge/Discharge Rates, High Temperature Behavior, Low Temperature Behavior

Fig. 2 Experimental Variables in the Preparation of Ni/Cd Battery Plates

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